anthraquinone and benzoquinone as the catalysts in the oxidation of anethol.

3. The importance of the maximum oxygen absorption rate has been emphasized as one of the most characteristic properties in all auto-oxidation phenomena.

* CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 44.

[1] "Homogeneous Catalysis" (a general discussion), *Trans. Faraday Soc.*, **24** (September, 1928).

[2] Dhar, *Proc. Acad. Amsterdam*, **23**, 1074 (1921).

[3] Moureu and Dufraisse, *Compt. rend.*, **176**, 624 (1923).

[4] Bäckström, *Trans. Faraday Soc.*, **24**, 602 (1928).

[5] Milas, *J. Phys. Chem.*, in press.

[6] Milas, these PROCEEDINGS, **14**, 844 (1928).

[7] Bennett and Willis, *J. Chem. Soc.*, **261** (February, 1929).

[8] Bäckström, *Medd. K. Vetenskapsakad. Nobelinst.*, **6**, 38 (1927).

[9] Kurt Meyer, *Ber.*, **42**, 1149 (1909).

UNIMOLECULAR REACTIONS

BY LOUIS S. KASSEL*

GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 224

Communicated May 27, 1929

Bourgin[1] has recently attempted to apply the new quantum mechanics to the problem of unimolecular reaction rates. There are some features of his work which are perhaps less satisfactory from the chemical standpoint than might be desired, and it is intended to examine these in more detail.

Bourgin assumes that the bond whose dissociation initiates the reaction has a potential energy function qualitatively similar to that of an alpha particle in a radioactive nucleus; that is, on one side there is a trough, A, whose shape is that of a deformed parabola; on the other is a relatively flat region, B, and between A and B there is a hump, that is, a maximum in the potential energy curve. Now on the quantum mechanics a system in the region A may leak through the hump into the region B provided it has as much energy as the new state will require; this is the change which the experimentalist will recognize as dissociation. Unlike the older theories, the quantum mechanics does not require the system to have as much energy as corresponds to the top of the hump. This mechanism gives the time-lag between activation and reaction which is necessary in any collisional activation theory of unimolecular reactions. Bourgin apparently assumes that the only effect of the other degrees of freedom

of the molecule, or at least the only important effect, will be to produce a potential energy curve of the required shape. He says, ". . . only the more complicated molecules, where extraordinary couplings may be expected, can exhibit the phenomenon of unimolecular reaction."

Now the great difficulty in accounting for the rates of unimolecular reactions has been to get great enough rates of activation; the rate of activation by collision is ordinarily calculated in accordance with the principle of microscopic reversibility by taking the product of the concentration of the activated molecules required by the Maxwell-Boltzmann distribution law and the number of times per second a molecule transfers internal energy to another molecule by collision. There are serious objections to assuming a value for this second factor which exceeds too greatly the number of collisions given by ordinary kinetic theory. The concentration of activated molecules was formerly taken as that given by the Maxwell-Boltzmann distribution law for systems with two squared terms in their energy function—for example, harmonic oscillators. The rates of activation calculated in this way were too small, the discrepancies being of the order of 10^5, even at moderate pressures.[2] By assuming on the other hand that activated molecules need only have sufficient internal energy, which may be distributed in any way among their various modes of vibration, a greatly increased concentration of activated molecules is obtained, and theories constructed on this basis have met with considerable success;[3] it is only in connection with the decomposition of nitrogen pentoxide at pressures well below 0.5 mm. that there is any serious discrepancy between theory and experiment, and at the present time there is still considerable uncertainty as to the actual behavior of the reaction in this pressure region.

Bourgin proposes to return to the older idea that an activated molecule is one in which some particular bond has energy greater than a critical value, and suggests that by assigning to this bond the type of potential energy curve described above, it may be possible to get a sufficient increase in the Maxwell-Boltzmann quota of activated molecules over that for harmonic oscillators to account for the experimental results. The present author has investigated somewhat the effect on the distribution law of making the oscillators anharmonic, and giving them a finite energy of dissociation, without having any hump in the potential energy curve; the calculations involved the use of semi-convergent series, and were never brought into a form suitable for publication;[4] there is very little doubt, however, that the effect on the distribution law was not great enough to be of any importance for these purposes. It is quite probable that a similar result will be found in Bourgin's case; it seems altogether unlikely than any factors of the order of 10^4 can be generated by a mere distortion of the potential energy curve.

There is also a further objection to Bourgin's treatment, more of a qualitative character. It may be granted that in complex molecules the potential energy curve will be deformed more than in simple ones, through there does not seem to be any obvious reason why it should have the particular shape Bourgin postulates. But in any case one should expect that the relevant potential energy curves for the substances azomethane and azo-isopropane would be quite similar, and hence, if there is no other effect of the molecular complexity, nearly the same results should be obtained in the decomposition of these two substances. Actually, Ramsperger[5] has found that the first order rate is maintained in the decomposition of the azo-isopropane at pressures where the rate constant for azomethane has decreased several-fold. In the type of theory used by Rice and Ramsperger, and the author, this difference finds a natural explanation in the greater number of degrees of freedom in the more complex molecule of azo-isopropane.

What seems to the author a more natural method of introducing the quantum mechanics into the problem is to retain the idea that the time-lag between activation and reaction is due to a necessity for the energy to get into the right place in the molecule, and to improve upon the calculation of the rate at which this change can take place. Some time ago, when it was first attempted to give a treatment of unimolecular reactions based on the old quantum theory, it was found necessary to include in the molecular model only oscillators of commensurable frequencies since otherwise energy exchanges could not occur.[6] It was pointed out that such a model could not be correct, but the explanation was not evident at that time. It now seems likely that the process of dissociation is a radiationless quantum jump from a level in the discrete spectrum of the molecule to a level in the continuous spectrum; the two spectra overlap, and the two levels involved have the same energy. The difficulties involved in any actual calculation on this basis are, of course, very great.

* NATIONAL RESEARCH FELLOW IN CHEMISTRY.

[1] D. G. Bourgin, *Proc. Nat. Acad. Sci.*, **15**, 357 (1929).

[2] Christiansen and Kramers, *Z. physik. Chem.*, **104**, 451 (1923); G. N. Lewis, *J. Am. Chem. Soc.*, **47**, 1508 (1925); R. C. Tolman, *Ibid.*, **47**, 1524 (1925).

[3] O. K. Rice and H. C. Ramsperger *J. Am. Chem. Soc.*, **49**, 1617 (1927); **50**, 617 (1928); O. K. Rice, *Proc. Nat. Acad. Sci.*, **14**, 114, 118 (1928); L. S. Kassel, *J. Phys. Chem.*, **32**, 225, 1065 (1928).

[4] See preliminary note: L. S. Kassel, *Proc. Nat. Acad. Sci.*, **14**, 29 (1928).

[5] H. C. Ramsperger, *J. Am. Chem. Soc.*, **50**, 714 (1928).

[6] L. S. Kassel, *J. Phys. Chem.*, **32**, 1065 (1928).